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(ONTARIO) DEPT OF CHEMISTRY M HAGA ET AL. 1984 TR-36
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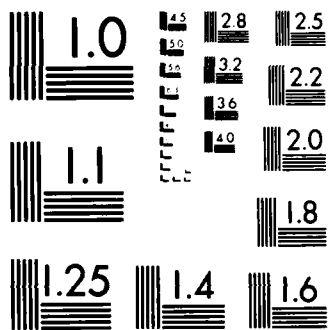
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Luminescence Quenching of The Tris(2,2'-bipyrazine) Ruthenium(II) Cation,
and its Monoprotonated Complex

BY

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20. Species in concentrated sulfuric acid. Original

Reagent, = inclusion

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Luminescence Quenching of The Tris(2,2'-bipyrazine) Ruthenium(II)
Cation, and its Monoprotonated Complex

Masa-aki Haga, Elaine S. Dodsworth, Goran Eryavec,
Penny Seymour and A.B.P. Lever*

Abstract

The MLCT excited state of the $\text{Ru}(\text{bipyrazine})_3^{2+}$ is quenched by a series of organic amines and methoxybenzenes, in acetonitrile solution. Linear Stern-Volmer plots were obtained, and various rate parameters were extracted from the data. The excited state is also quenched in neutral aqueous solution by a range of metal ions and complexes. Rate constants for both oxidative and reductive quenching mechanisms were obtained. In general the rates are faster for this ion than for the corresponding $\text{Ru}(\text{bipyridine})_3^{2+}$ excited state. Similar data were also obtained for the monoprotonated complex in 2M sulfuric acid and the hexaprotonated species in concentrated sulfuric acid.

Introduction

The excited-state chemistry of $\text{Ru}(\text{bipy})_3^{2+}$ (bipy = 2,2'-bipyridine) has been extensively investigated during the past decade.¹ Excited states may undergo various bimolecular processes, namely (1) energy transfer, (2) quenching by oxidative electron transfer, (3)

quenching by reductive electron transfer, and (4) excited-state proton transfer. With appropriate choice of systems the $\text{Ru}(\text{bipy})_3^{2+}$ cation may undergo processes (1)-(3).¹⁻³ These studies have been extended to the photochemical decomposition of water into hydrogen and oxygen by using $\text{Ru}(\text{bipy})_3^{2+}$ as a sensitizer.⁴

Recently, we have shown that the analogous $\text{Ru}(\text{bpz})_3^{2+}$ cation ($\text{bpz} = 2,2'$ -bipyrazine)⁵ is an excellent photocatalyst for methyl viologen (MV^{2+}) reduction. Table I shows a comparison of the properties of the two complexes. The metal to ligand charge transfer (MLCT) band of $\text{Ru}(\text{bpz})_3^{2+}$ is slightly shifted to higher energy and the lifetime of the emissive state is slightly longer than that of $\text{Ru}(\text{bipy})_3^{2+}$ in water. A major difference between the two systems lies in their redox potentials, those of $\text{Ru}(\text{bpz})_3^{2+}$ being shifted 0.5V positive relative to those of $\text{Ru}(\text{bipy})_3^{2+}$. Furthermore, the $\text{Ru}(\text{bpz})_3^{2+}$ cation has six peripheral uncoordinated nitrogen atoms which can be protonated step by step in sulfuric acid.⁶ We report here the systematic bimolecular quenching of $\text{Ru}(\text{bpz})_3^{2+}$ and its monoprotonated complex by simple ions and organic compounds.

Experimental

Materials $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$,⁷ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$,⁷ $\text{Ru}(\text{bpz})_3\text{Cl}_2$,⁵
 $[\text{Ru}(\text{bpz})_3](\text{PF}_6)_2$ ⁵ and $\text{Ru}(\text{bipy})_3\text{Cl}_2$ ⁸ were synthesized and purified as described previously. H_2SO_4 , KCl , KBr , KI , AgNO_3 , KNO_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$ were all analytical reagent grade. A loan of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ from the Johnson Matthey Company is

gratefully acknowledged. N,N'-Diphenyl-p-phenylenediamine was purchased from Fisher Scientific Co., and recrystallized from benzene. All other organic quenchers were purchased from Aldrich. Aniline, N,N-dimethylaniline and N,N-dimethyl-p-toluidine were purified by vacuum distillation before use. Phenothiazine, diphenylamine, and triphenylamine were recrystallized from ethanol. A series of methoxybenzenes were used without further purification.

Water doubly distilled over KMnO_4 was used to make up all solutions. Acetonitrile for quenching measurements was dried over P_2O_5 and distilled before use. Tetrabutylammonium perchlorate (Eastman) (TBAP) was recrystallized from ethanol and vacuum dried.

Luminescence Quenching Measurements

Emission spectra were recorded with a Varian SF-330 spectrofluorimeter. The exciting wavelength was 423nm and the emission intensity was monitored at the wavelengths 595nm (neutral complex), 717nm (monoprotonated complex) and 620nm (hexaprotonated complex). In neutral solution and in CH_3CN the concentrations of $\text{Ru}(\text{bpz})_3^{2+}$ and the quencher were about 10^{-5} M and $(10^{-2}-10^{-6})$ M, respectively. The ionic strength of solutions was adjusted to 0.1M with TBAP in acetonitrile, 1M with KCl in neutral aqueous solution, and 2M with sulfuric acid in acidic aqueous solutions. 1M KNO_3 was used instead of 1M KCl for the quenching experiment with the Ag^+ ion. For the experiments in CH_3CN , $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ was used because of its higher solubility.

In a typical experiment, the appropriate quenchers were added in microlitre 'spikes' to the $\text{Ru}(\text{bpz})_3^{2+}$ solution in a quartz or Pyrex

cuvette closed by a rubber serum cap. The solutions were bubble degassed with dry nitrogen for at least 15 min. The emission intensities were corrected for absorption of the incident light by the quenchers, using the following equation.⁹

$$\left(\frac{I_o}{I}\right)_{\text{corr}} = \left(\frac{I_o}{I}\right)_{\text{app}} \left[\frac{1 - 10^{-(A_D + A_Q)l}}{1 - 10^{-A_D l}} \right] \frac{A_D}{A_D + A_Q} \cdot 10^{-A_Q' l'}$$

where $(I_o/I)_{\text{app}}$ is the observed ratio of luminescence intensity in an unquenched solution to that in a quenched solution, and $(I_o/I)_{\text{corr}}$ is the ratio corrected for the inner filter effect. A_D and A_Q are the absorbances at the exciting wavelength for $\text{Ru}(\text{bpz})_3^{2+}$ and the quencher, respectively. A_Q' is the absorbance of the quencher at the emission wavelength, l is the excitation path length within the cell, and l' is the effective path length for re-absorption of the emitted radiation, estimated to be 0.5cm. For each quencher, the luminescence intensity was measured with at least four different quencher concentrations. Several sets of quenching experiments were carried out and quenching constants are averages obtained from the separate experiments.

Lifetime and lifetime quenching measurements were carried out using a York University constructed 0.5MW pulsed nitrogen laser and a Princeton Applied Research (PAR) Model 162 boxcar averager with a Model 165 gated integrator. Absorption spectra were recorded on a Perkin-Elmer Hitachi Model 340 microprocessor spectrometer.

Formation of ion pair complexes:- $[\text{Ru}(\text{bpz})_3]_2[\text{Fe}(\text{CN})_6] \cdot 12\text{H}_2\text{O}$

Concentrated solutions of $\text{Ru}(\text{bpz})_3\text{Cl}_2$ and $\text{K}_4\text{Fe}(\text{CN})_6$ were mixed together using an approximate 1:1 molar ratio, in water. A dark copper colored crystalline precipitate formed immediately. The product was recrystallised from hot water yielding black plate-like crystals and a green filtrate. The infrared spectrum shows $\nu(\text{CN})$ stretching vibrations at 2022, 2031 cm^{-1} . Anal. C,H,N,Fe. $[\text{Ru}(\text{bpz})_3]_3[\text{Fe}(\text{CN})_6]_2 \cdot 22\text{H}_2\text{O}$ Prepared as above but using $\text{K}_3\text{Fe}(\text{CN})_6$. An orange brown precipitate was recrystallised to yield orange-brown flaky crystals. The infrared spectrum shows $\nu(\text{CN})$ stretching vibrations at 2108, 2113 cm^{-1} . Anal, C,H,N. $[\text{Ru}(\text{bpz})_3]_3[\text{Co}(\text{CN})_6]_2 \cdot 22\text{H}_2\text{O}$ Prepared as above but using $\text{K}_3\text{Co}(\text{CN})_6$. An orange precipitate is formed. The infrared spectrum shows $\nu(\text{CN})$ stretching vibrations at 2114 cm^{-1} . Anal, C,H,N.

Results and Discussion

1) Quenching in CH_3CN by aromatic amines and methoxybenzenes

The emission intensities gave linear Stern-Volmer plots as a function of the quencher concentrations for all systems. The quenching rate constants, k_q , were calculated from equation (1),

$$\left(\frac{I_0}{I}\right) = 1 + K_{SV}[Q] = 1 + \tau_0 k_q [Q] \quad (1)$$

where I_0 and I are the emission intensities of a solution of $\text{Ru}(\text{bpz})_3^{2+}$ in the absence and presence of quencher, respectively. τ_0 is the lifetime of $\text{Ru}(\text{bpz})_3^{2+}$ with no added quencher (Table I). The bimolecular quenching rate constants are shown in Table II.

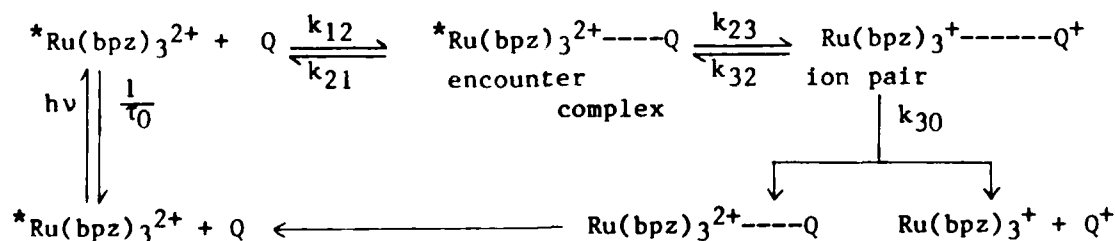
Bimolecular quenching may take place by various mechanisms. However, where rate constants are greater than $10^7 \text{ M}^{-1}\text{s}^{-1}$ only energy and electron transfer processes need to be considered. Amines and

methoxybenzenes do not have appropriate low-lying excited states, so that energy transfer quenching of $\text{Ru}(\text{bpz})_3^{2+}$ in CH_3CN is energetically unfavourable. In this case, the k_q values increase with decreasing oxidation potential of the quenchers (Table II). Thus the most probable quenching mechanism for reaction of the $\text{Ru}(\text{bpz})_3^{2+}$ cation with amines and methoxybenzenes is reductive quenching.

The theory of electron transfer quenching¹³, is based on the relationship between the quenching rate constants and free energy change of outer-sphere electron transfer.¹⁰⁻¹⁵ Only a brief summary will be presented here. The reaction scheme for electron transfer quenching can be described by Scheme 1, where k_{12} is the diffusion rate constant, k_{21} is the rate constant for dissociation of the precursor complex, k_{23} and k_{32} are rate constants for electron transfer between encounter complex and ion pair, and k_{30} is a combined rate constant for disappearance of the ion pair leading to net quenching.

Rehm-Weller Mechanism

SCHEME 1



The driving force for quenching may be written in terms of ΔG_{23} , where, in the case here of quenching by amines (Q), reductive quenching is involved:^{10,12}

$$\Delta G_{23} = E_{1/2}[Q^+/Q] - E_{1/2}[Ru^{2+*}/Ru^+] + w_p - w_r \quad (2)$$

where w_p and w_r are the work terms required to bring the products (Ru^+ , Q^+) and reactants (Ru^{2+*} , Q) together at the separation distance in the encounter complex. Since the amines are uncharged, w_r may be neglected and w_p is small; we assume a value of 0.01V.¹²

The free energy of activation for electron transfer, ΔG^\ddagger_{23} , may be related to this driving force by various different equations¹⁶ but they generally give very similar results. We use here the equation derived by Agmon and Levine:¹⁷

$$\Delta G^\ddagger_{23} = \Delta G_{23} + (\Delta G^\ddagger(0)/\ln 2) \ln[1 + \exp(-\Delta G_{23}) \ln 2 / \Delta G^\ddagger(0)] \quad (3)$$

where $\Delta G^\ddagger(0)$ is the free energy of activation for $\Delta G_{23} = 0$, and is the so-called "intrinsic barrier" or reorganisation energy.

We are concerned here with whether our experimental data can be fitted to reasonable values of these various parameters, based upon previous experience in the bipyridine series. Values of $E_{1/2}[Q^+/Q]$ are available in the literature. A value for $E_{1/2}[Ru^{2+*}/Ru^+]$ can be estimated from the ground state potential and the emission energy via:-

$$E_{1/2}[Ru^{2+*}/Ru^+] = E_{0,0} + E_{1/2}[Ru^{2+}/Ru^+]$$

also

$$E_{1/2}[Ru^{3+}/Ru^{2+*}] = E_{1/2}[Ru^{3+}/Ru^{2+}] - E_{0,0}$$

(4)

This last equation has some uncertainty depending upon whether all the spectroscopic energy in the excited state can be used as redox energy, and generally predicts a value which may be too low by up to 0.1V.

The relationship between the observed quenching rate constants and the above mentioned parameters may be written:-¹³

$$k_q = k_{12} / [1 + (k_{12} / \Delta V k_{30}) (\exp(\Delta G_{23}^{\#} / RT) + \exp(\Delta G_{23} / RT))] \quad (5)$$

where $\Delta V = k_{12} / k_{21}$ is the encounter volume, $k_{12} = k_d$ (the diffusion rate constant), and k_q is the observed rate constant. In common with Balzani,¹⁰ in a study of the quenching of $\text{Cr}(\text{bipy})_3^{3+}$ and $\text{Ru}(\text{bipy})_3^{2+}$ with aromatic amines, the values $k_d = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $\Delta V k_{30} = 8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ were assumed. Values of $E_{1/2}[\text{Ru}(\text{bpz})_3^{2+*} / \text{Ru}(\text{bpz})_3^{+}]$ and $\Delta G^{\#}(0)$ (cf eqn.(3)) were then sought by obtaining a best fit between observed and calculated rate constants. There is some correlation in fit between these two variables and it does not seem possible, by this method alone, to define each parameter independently. In the case of the $E_{1/2}[\text{Ru}(\text{bipy})_3^{2+*} / \text{Ru}(\text{bipy})_3^{+}]$ couple, the accepted value is some 0.08V higher than predicted by eqn.(4).¹² We assume a similar situation with the bipyrazine complex and fix $E_{1/2}[\text{Ru}(\text{bpz})_3^{2+*} / \text{Ru}(\text{bpz})_3^{+}] = 1.45\text{V}$. With this value an acceptable fit between observed and calculated k_q values (Fig.1) is seen, with $\Delta G^{\#}(0) = 0.24\text{eV}$ (5.5 kcal/mol). This compares with ca 4 kcal/mol for $\text{Ru}(\text{bipy})_3^{2+}$.¹² The parameters correlate positively; if the electrode potential is slightly over-estimated, so will be the reorganisation energy parameter. Note that permitting k_d and $\Delta V k_{30}$ to vary from the assumed values offered no improvement of fit; the

values assumed seem acceptable.

Thus the bipyrazine system behaves similarly to the bipyridine system but with a much larger value for the excited state potential couple, as previously proposed.

Using the Marcus "cross reaction" equation^{12,18,19} one may obtain the self-exchange rate of the ruthenium couple (k_{ii}) using the expression:-

$$RT \ln k_q'(0) = 0.5 RT \ln(k_{ii} k_{jj}) + (\text{work terms}) \quad (6)$$

where the work terms, to bring reactants together, are small and are neglected here, and k_{jj} is the self-exchange rate of the quencher. The term $k_q'(0)$ is the quenching rate (corrected for diffusion) when the driving force is zero. This value can be derived from our data, as the rate when $\Delta G_{23} = 0$ (eqn.5), i.e. when $E_{1/2}(Q^+/Q) = 1.45V$. Thus (Table II) $RT \ln k_q'(0) = RT \ln k_q = 0.46$ (the correction for diffusion is negligible), and assuming with Meyer an average quencher self-exchange rate of $8.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ in this medium, eqn.(6) yields a self-exchange rate for the $\text{Ru}(\text{bpz})_3^{2+}$ system of $4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. This is an approximate lower limit for this exchange rate. The upper limit could be derived on the basis that the true excited redox potential for the $[\text{Ru}(\text{bpz})_3^{2+*}/\text{Ru}(\text{bpz})_3^+]$ couple will not be less than 1.37V. This yields, using the quenching data, a self-exchange rate constant of $4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. The corresponding value for the bipyridine-ruthenium system is ca. $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹² Thus the rate for the bipyrazine system appears to be slower, even allowing for possible experimental error.

Table I

Photophysical, Photochemical and Electrochemical Data

	$\text{Ru}(\text{bipy})_3^{2+}$	$\text{Ru}(\text{bpz})_3^{2+}$	$\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$	$\text{Ru}(\text{bpzH})_3^{8+}$
Absorption λ_{max} , nm in H_2O	452	441 (443) ^a	475	458
Emission λ_{max} , nm	607	595 (591) ^a	717	620
Lifetime τ , ns	620 ($\phi=0.042$)	920 (1MKCl) 740 (CH_3CN)	50 ($2\text{MH}_2\text{SO}_4$)	520 (conc. H_2SO_4)
ϕ (photoanation) in $\text{CH}_3\text{CN}-\text{Cl}^-$	0.01	0.37	-	-
Mechanism of quenching in $\text{MV}^{2+}/\text{TEOA}$ system	Oxidative quenching by MV^{2+}	reductive quenching by TEOA	-	-
$E(\text{RuL}_3^{3+}/^{2+})^b$ V vs SCE in CH_3CN	1.29	1.86(1.95) ^c	+2.27V ^d	
$E(\text{RuL}_3^{2+}/^+)$	-1.33	-0.80(-0.71) ^c	-0.28V ^d	
$E(\text{RuL}_3^{3+}/^{2+*})$	-0.81	-0.26 ^d	+0.55V ^d	
$E(\text{RuL}_3^{2+*}/^+)$	+0.77	+1.45	+1.44V ^d	

a) In CH_3CN b) vs SCE in CH_3CN

c) Data from ref. 5d.

d) Calculated.

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21. We assume here a value of r equal to the sum of the radii of the two reactants, $r_A + r_D$. The following values of radii have been used for calculation: $\text{Ru}(\text{bpz})_3^{2+}$, 7.1 Å; Fe^{2+} and Fe^{3+} , 3.5 Å; Cu^{2+} , 3.8 Å; I^- , 2.16 Å; $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, 3.8 Å; $\text{Co}(\text{NH}_3)_6^{3+}$, 3.5 Å; $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, 4 Å. Eqn. 6^{20c}: $k_0 = \frac{8RT}{3\eta} \cdot \frac{b/r}{e^{\frac{b}{r}} - 1}$ where $b = \frac{Z_A Z_D e^2}{\epsilon kT 4\pi\epsilon_0}$
- and all constants are in S.I. units.
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Formation of Donor-Acceptor Ion Pairs

The possibility of complex formation between the positively charged $\text{Ru}(\text{bpz})_3^{2+}$ ion and negative quenchers such as the hexacyano ions could not be neglected, especially as there is much evidence in the literature for similar types of species.^{34,35} It is possible to isolate complexes of the type $[\text{Ru}(\text{bpz})_3]_2\text{Fe}(\text{CN})_6$ and $[\text{Ru}(\text{bpz})_3]_3[\text{M}(\text{CN})_6]_2$ ($\text{M} = \text{Fe}(\text{III}), \text{Co}(\text{III})$) but this does not require that these ions interact significantly in dilute solution. Indeed solutions of these complexes show visible region CT spectra typical of the ruthenium(II) component. In the solid state the complexes are intensely colored, have FTIR $\nu(\text{CN})$ frequencies differing from the simple alkali metal hexacyano anions, and presumably do involve some charge transfer under these conditions. A strong solution of the ferricyanide ion pair in aqueous solution shows a broad band centered about $15,150(670) \text{ cm}^{-1}$. This is not present in either of the components and may be an intervalence transition.³³⁻³⁵

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that under the strongly acidic conditions, dissociation of cyanide ion may be fast enough to provide an alternate quenching mechanism.³² Alternatively, in view of the high negative charge on the quencher and high positive charge on the excited ruthenium species, some kind of exciplex may be formed. Further study of these two last systems is in progress.

iv) Quenching of hexaprotonated $[\text{Ru}(\text{bpzH}_2)_3]^{8+}$ in concentrated sulfuric acid.

No electrochemical data exist for this species in concentrated sulfuric acid. However the ground state potentials will be more positive than those for the monoprotonated material. Moreover the emission is at a higher energy (2.0 eV). Thus the excited hexaprotonated species should be a stronger oxidising agent than the excited monoprotonated species, and perhaps a comparable reducing agent.

It is difficult to adequately probe the photophysics of this species because concentrated sulfuric acid is such an unforgiving solvent. Most quenchers will be protonated by this medium, resulting in an increase in their redox potentials. Even simple metal aquo-ions are likely to be modified. Thus most quenchers will carry a positive charge and their approach to the excited hexaprotonated species is likely to be greatly inhibited by charge repulsion. Moreover the solution is very viscous, reducing the diffusion rates. Thus greatly reduced quenching rates are expected, and are observed (Table III).

hexacyanoiron species, we have simply assumed a Nernstian dependence to derive appropriate numbers. This is not expected to be far from the true situation.

Compared with the neutral species, oxidative quenching of the monoprotonated species should be much more difficult (slower), while driving forces for reductive quenching of both species are comparable. For the simple Fe(II) and Fe(III), and for the ferrocyanide ions this expectation is achieved. For Cu(II) we anticipate oxidative quenching and hence a marked reduction in rate. Such a reduction is observed but it is small. The calculated driving force is now strongly uphill, yet considerable quenching is observed.

It is possible that there has been a switch to a dominant energy transfer mechanism. The aquo Cu(II) ion has a broad d-d absorption centred near $12,500\text{ cm}^{-1}$,³³ relatively close to the emission of the protonated $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$ ion at $13,800\text{ cm}^{-1}$. Overlap between donor and acceptor should be good and thus an energy transfer mechanism may be appropriate at least in acid solution.

The strong affinity for nitrogen ligands of the copper ion, and the higher basicity of the excited ruthenium-bipyrazine entity, may result in some binding of the Cu(II) to the excited state species, facilitating quenching.

The ferricyanide ion is a much more effective quencher than anticipated. Oxidative quenching should be greatly inhibited and there are no low lying transitions^{27a} to allow energy transfer. Formation of an iron(IV) species may be occurring (reductive quenching) but we know of no evidence for such a species in strong acidic media. Quenching by free cyanide ion would be much more effective than quenching by ferricyanide ion, and it is possible

this is not the case for the ground state species; it is therefore difficult to measure the ground state redox potential of the monoprotinated species directly. It may be estimated via the Nernst equation, viz:-

$$E = E^{\circ} + 2.303(RT/nF)pH \quad (10)$$

Assuming $pH = -0.3$ in $2M H_2SO_4$, and the E° values reported in Table I for the unprotonated species, the data for the monoprotinated species, which are also shown in Table I, are derived from eqn.(10).

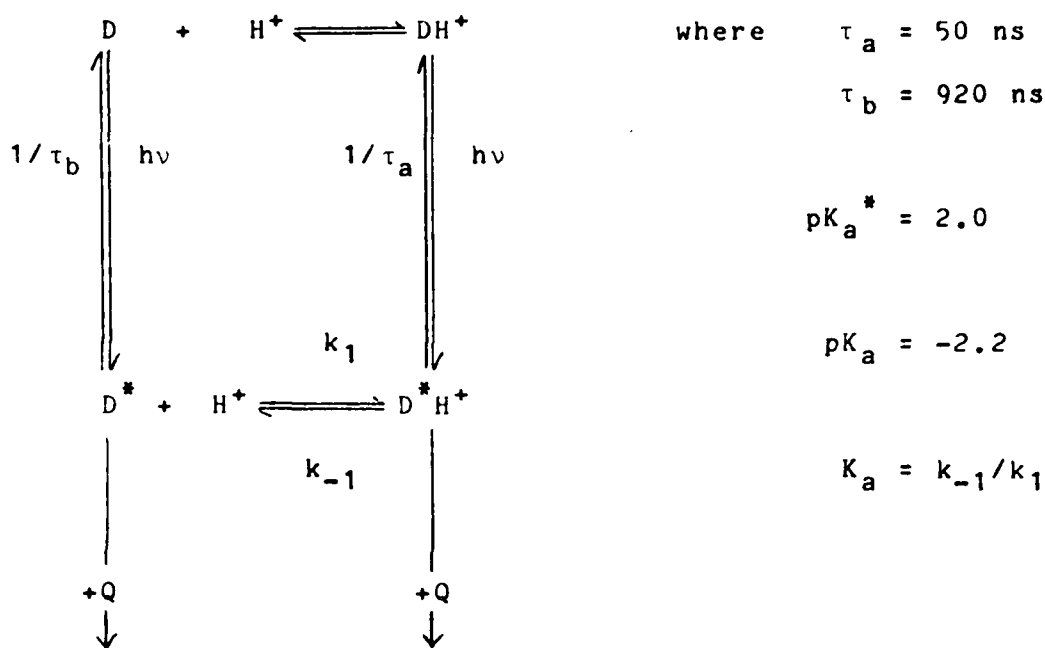
The monoprotinated species emits at $13,900 \text{ cm}^{-1}$ (1.72eV), and, assuming this represents the (0,0) transition, use of eqn.(4) provides estimates for the excited state potentials also shown in Table I.

Thus the monoprotinated species is seen to be a much weaker reducing agent than the unprotonated species, but a comparable oxidising agent. It had been hoped that this species would have been a much stronger oxidising agent in the excited state, because of the Nernstian shift in potentials due to the extra positive charge. That it is not so, is due almost entirely to the significant shift to lower energy of the emission frequency.

The quenching rate constants from Stern-Volmer analysis are shown in Table III and the calculated driving forces are shown in Table IV. To calculate the driving forces for the $Cu(II)$, $Fe(II)$, and $Fe(III)$ aquo-ions, which are not expected to be protonated in $2M H_2SO_4$, the same electrode potentials were used as for the neutral species calculations. However the hexacyano anions will be protonated in acidic media and although some data are available in the literature³² for the redox potentials of protonated

possible to probe their electron transfer photochemistry.

However, it is necessary to be sure that the protonation equilibrium is fully achieved prior to deactivation by the quencher. The following situation (9) may prevail for the monoprotonated species:-



$$\text{where } \tau_a = 50 \text{ ns}$$

$$\tau_b = 920 \text{ ns}$$

$$\text{pK}_a^* = 2.0$$

$$\text{pK}_a = -2.2$$

$$K_a = k_{-1}/k_1$$

(9)

Using the reported pK_a^* value and an assumed value of $k_{-1} > 10\tau_a^{-1}$ ($> 2 \times 10^8 \text{ s}^{-1}$) for the deprotonation constant, and following the discussion for $\text{Ir}(\text{bipy})_2(\text{bipyH})^{3+}$ ³⁰, the second order rate constant for protonation, k_1 , would be estimated to be $> 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. On the other hand if it were assumed that the deactivation were faster than the acid-base equilibrium, say $k_{-1} < 0.1\tau_a^{-1}$, then $k_1 < 2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. Since rate constants for protonation processes are typically diffusion controlled ($10^{10} - 10^{11} \text{ M}^{-1}\text{s}^{-1}$)³¹, the value estimated for this latter situation is far too slow. One may therefore conclude that the excited state protonation equilibrium is established much faster than decay back to the ground state.

Although the excited state species in $2\text{M H}_2\text{SO}_4$ is protonated,

quenching rate constant for the $[\text{Fe}(\text{CN})_6]^{4-}$ ion is a maximum of $2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ which may be indicative of some static quenching. However there is a slow thermal chemical reaction between the $\text{Ru}(\text{bpz})_3^{2+}$ and ferrocyanide ions in the presence of chloride ion; this undeniably complicates the issue, and may also be responsible for the apparently much greater than diffusion rate quenching observed for this ion.

Comparison of these data with the quenching of $\text{Ru}(\text{bipy})_3^{2+}$ is illuminating (Table V). In general the $\text{Ru}(\text{bipy})_3^{2+}$ quenching rates are at least one order of magnitude slower than those of the bipyrazine species, for both oxidative and reductive quenching processes. The only exception is for quenching with the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion (oxidative). Since the bipyrazine species is a stronger oxidising agent in the excited state than the bipyridine species, reductive quenching is expected to proceed more rapidly. Certainly the rates for oxidation of the various amine species discussed in the previous section, are significantly more rapid with $\text{Ru}(\text{bpz})_3^{2+}$ than with $\text{Ru}(\text{bipy})_3^{2+}$.^{10,11}

The excited ruthenium tris(bipyridine) system is, however, a significantly better reducing agent than the bipyrazine analog and it is difficult to understand why oxidative quenching should generally be slower with this species.

iii) Quenching in Acidic Aqueous Media by Metal Ions

In 2 M H_2SO_4 the most important excited state species is $[\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}]^*$. In concentrated sulfuric acid, the ground state species is the hexaprotonated $\text{Ru}(\text{bpzH}_2)_3^{8+}$ (no doubt heavily ion-paired)⁶, but the predominant excited state species is probably pentaprotonated. Both these excited species emit, so that it is

in the nature of the quenchers, especially the variation in charge.

The Co(II) ion has uphill driving forces for both reductive and oxidative quenching, thereby explaining its lack of reaction. Mn(II) has a small downhill driving force for reductive quenching but it is evidently not enough, in view of the positive charge on the quencher, for any quenching to be observed. The absence of oxidative quenching by Ag(I) is, however, puzzling.

We conclude that the dominant quenching mechanism is as shown in (8) although we recognise that this does not constitute a proof. However comparing these data with those for the $\text{Ru}(\text{bipy})_3^{2+}$ ion, shows that the mechanisms proposed here are identical to those proposed or proven with the tris(bipyridine) ion, specifically for $\text{Fe}(\text{III})^{24}$, $\text{Cu}(\text{II})^{25}$, $[\text{Fe}(\text{CN})_6]^{4-}$ ^{26,27}, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ^{28,29}.

It is difficult to compare these data (Table III) in depth because of the varying charges and types of quencher. However note that the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, I^- , and $[\text{Fe}(\text{CN})_6]^{n-}$ ($n = 3,4$) ions all quench at the diffusion rate. The last three are undoubtedly assisted by their negative charge while the first has a very substantial driving force for quenching. Other ions quench at a lower than diffusion rate generally because of lower driving forces and their positive charge; however note that the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion has an unexpectedly low k_q value in this context.

The data in Table III were obtained via intensity quenching. Two systems were also studied by lifetime quenching. The $[\text{Fe}(\text{CN})_6]^{2-}$ ion yielded a lifetime quenching rate constant of $40 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, essentially the same as that shown in Table III; thus static quenching is not significant despite the interaction in concentrated solution (see below). On the other hand, the lifetime

while the corresponding equation for oxidative quenching is:-

$$\Delta G_{23} = -E_{1/2}[Q^+/Q] + E_{1/2}[Ru^{3+}/Ru^{2+}] + w_p + w_r \quad (7)$$

where a value of $-0.26V$ is calculated for $E_{1/2}[Ru(bpz)_3^{3+}/Ru(bpz)_3^{2+}]$ on the basis of the ground state potential and excited state energy (Table I).

Table IV includes the driving forces for both oxidative and reductive quenching for the various quenchers at pH 7 (and also -0.3). They were calculated using the excited state potentials shown in Table I and the standard quencher potentials, $E[Q^+/Q]$ and $E[Q/Q^-]$ (in the presence where relevant, such as $Cu(II)$, of chloride ion). In general, considering the pH=7 data, one of these processes dominates. Choosing the most downhill process as the most probable mechanism, the observed rate constants tend to increase with the driving force. Thus, for reductive quenching:-

	$[Fe(CN)_6]^{4-}$	I^-	$[Fe(H_2O)_6]^{2+}$
k_q	100	70	$6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
driving force	1.33	1.14	0.92V

(8a)

and for oxidative quenching:-

	$Fe(H_2O)_6^{3+}$	$Fe(CN)_6^{3-}$	$Cu(H_2O)_4^{2+}$	$Co(NH_3)_5Cl^{2+}$	$Co(NH_3)_6^{3+}$
k_q	105	56	5	5.7	$1.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
driving force	0.79	0.38	0.54	0.34	0.12V

(8b)

An exact correlation should not be expected in view of the variation

ii) Quenching in Neutral Aqueous Media by Metal Ions

Many metal cations, and several anions, will quench the luminescence of the $\text{Ru}(\text{bpz})_3^{2+}$ ion and a brief survey of these has been made, both in neutral and acidic media. In the latter case, the protonated ruthenium-bipyrazine system is involved and is discussed separately below. No quenching was observed with Cl^- , Br^- , $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or Ag^+ (this last ion in nitrate medium), under neutral or acidic conditions. However $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{n-}$ ($n=2,3$), $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ were effective quenchers both in neutral and acidic media. The $[\text{Co}(\text{CN})_6]^{3-}$ ion was also an effective quencher but the Stern-Volmer plots were non-linear and further study was postponed. The other complexes yielded linear Stern-Volmer plots and the rate constants obtained therefrom are shown in Table III. Table III also contains the hypothetical diffusion rates corrected for ionic strength (1M KCl) using Debye-Huckel expressions in the literature.^{20,21}

The lowest excited state of $\text{Ru}(\text{bpz})_3^{2+}$ lies at $16,800\text{ cm}^{-1}$ and for energy transfer there should be some overlap between the emission band of the donor (ruthenium) and the lower energy absorption band of the acceptor (quencher) excited state;²² there are also some spin selection rules.²³ While energy transfer has been considered in the past, as a mechanism for the quenching of the excited state of the $\text{Ru}(\text{bipy})_3^{2+}$ ion by quenchers of this type, it is not now considered likely in most cases.²⁴⁻²⁹ Except in one or two cases, as noted below, it is probably not important in the bipyrazine system.

The driving force for reductive quenching is as shown in (2),

Table II

Quenching Rate Constants For $\text{Ru}(\text{bpz})_3^{2+}$ in Acetonitrile $(\mu=0.1 \text{ M}, 22^\circ\text{C})$

Quencher	$E(Q/Q^+), \text{V vs SCE}$ [10-12]	$k_q, \text{M}^{-1} \text{s}^{-1}$	$RT \ln k_q^a$ (calc.)	$RT \ln k_q$ (observed)
1. N,N'Diphenyl- γ -Phenylene-diamine	0.35	1.1×10^{10}	.591	.593
2. Phenothiazine	0.53	7.9×10^9	.591	.586
3. N,N-Dimethyl-p-Toluidine	0.71	8.6×10^9	.590	.588
4. N,N-Dimethylaniline	0.81	8.4×10^9	.589	.587
5. Diphenylamine	0.83	5.6×10^9	.589	.577
6. Aniline	0.98	5.2×10^9	.585	.575
7. Triphenylamine	1.06	6.2×10^9	.580	.579
8. 1,2,4-Trimethoxybenzene	1.12	2.9×10^9	.574	.560
9. 1,4-Dimethoxybenzene	1.34	8.6×10^8	.514	.529
10. 1,2,3-Trimethoxybenzene	1.42	6.5×10^7	.478	.462
11. 1,2-Dimethoxybenzene	1.45	1.7×10^8	.464	.486
12. 1,3,5-Trimethoxybenzene	1.49	2.7×10^7	.444	.440

(a) See text for parameters fitted to eqn. (5).

Table III

Quenching Rate Constants for $\text{Ru}(\text{bpz})_3^{2+}$ and Protonated Species

Quencher	$\text{Ru}(\text{bpz})_3^{2+}$ (a)		$\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$ (b)		$\text{Ru}(\text{bpzH}_2)_3^{8+}$ (c)		
	$10^{-8} k_q$ $\text{M}^{-1} \text{s}^{-1}$	$10^{-8} k_d$ (d) $\text{M}^{-1} \text{s}^{-1}$	Reaction (e) $\text{M}^{-1} \text{s}^{-1}$	$10^{-8} k_d$ (d) $\text{M}^{-1} \text{s}^{-1}$	Reaction (e) $10^{-8} k_q$ $\text{M}^{-1} \text{s}^{-1}$		
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$ (f)	6	100	2	7	115	2	1.1
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$ (g)	105	100	3	1	130	3	0.1
$\text{Cu}(\text{H}_2\text{O})_4^{2+}$	5	100	3	5	115	1	0.3
I^-	70	40	2				
$\text{Fe}(\text{CN})_6^{4-}$	100	6	2	53	5		
$\text{Fe}(\text{CN})_6^{3-}$	56	12	3	410	10		
$\text{Co}(\text{NH}_3)_6^{3+}$	1.3	100	3				
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	5.7	100	3				

a) In aqueous solution, $\mu=1.0 \text{ M}(\text{KCl})$, 20° . b) In 2 M sulfuric acid. c) In conc. sulfuric acid. d) Calculated rate constants for diffusion-controlled quenching. The Debye-Huckel expressions are not a good model at high ionic strength so values for 2 M sulfuric acid are only approximate. e) Reaction responsible for quenching; energy transfer (1), reductive quenching (2), and oxidative quenching (3). f) Ferrous sulfate was used as a quencher. The use of ferrous ammonium sulfate with the unprotonated ruthenium species yielded a quenching rate constant of $20 \times 10^{-8} \text{ M}^{-1}\text{s}^{-1}$. g) Ferric ammonium sulfate was used as a quencher.

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Table IV

THERMODYNAMIC DRIVING FORCES (eV) FOR REDUCTIVE AND OXIDATIVE QUENCHING^a

Species	pH	Oxidative quenching	Reductive quenching
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	7	-0.42	0.92
	-0.3	-1.23	0.91
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	7	0.79	0.19
	-0.3	-0.02	0.18
$[\text{Fe}(\text{CN})_6]^{4-}$	7	-0.48	1.33
	-0.3	-1.29	1.32
	-0.3	-0.86*	0.89*
$[\text{Fe}(\text{CN})_6]^{3-}$	7	0.38	< 0.19
	-0.3	-0.43	< 0.18
	-0.3	0*	<-0.25*
$\text{Cu}(\text{H}_2\text{O})_4^{2+}$	7	0.54	-0.11
	-0.3	-0.252	<-0.12
$[\text{Co}(\text{NH}_3)_6]^{3+}$	7	0.12	<-0.11
	-0.3	-0.69	<-0.12
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+b}$	7	0.34	<-0.11
	-0.3	-0.12	<-0.5

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Table IV cont.

Species	pH	Oxidative quenching	Reductive quenching
I ⁻	7	<-1.5	1.14
Co(H ₂ O) ₆ ²⁺	7	-0.26	-0.12
	-0.3	-1.07	-0.13
Mn(H ₂ O) ₆ ²⁺	7	-1.16	0.18
	-0.3	-1.97	0.17
Ag(I)/NO ₃ ⁻	7	0.82	-0.29
	-0.3	0.01	-0.30

a) The < sign means more negative than. A * star signifies corrected for Nerstian shift. Mⁿ⁺/Mⁿ⁻¹⁺ couples taken from Huheey, J.E. "Inorganic Chemistry", 1972 edn p.258 et seq. b) from Curtis, N.J.; Lawrance, G.A.; Sargeson, A.M., Aus.J.Chem., 1983, 36, 1327. Note that, with respect to neutral solution, the corresponding driving forces for quenching of the Ru(bipy)₃²⁺ ion, are approximately 0.5V greater for oxidative quenching and approximately 0.7V smaller for reductive quenching.

15/11/84

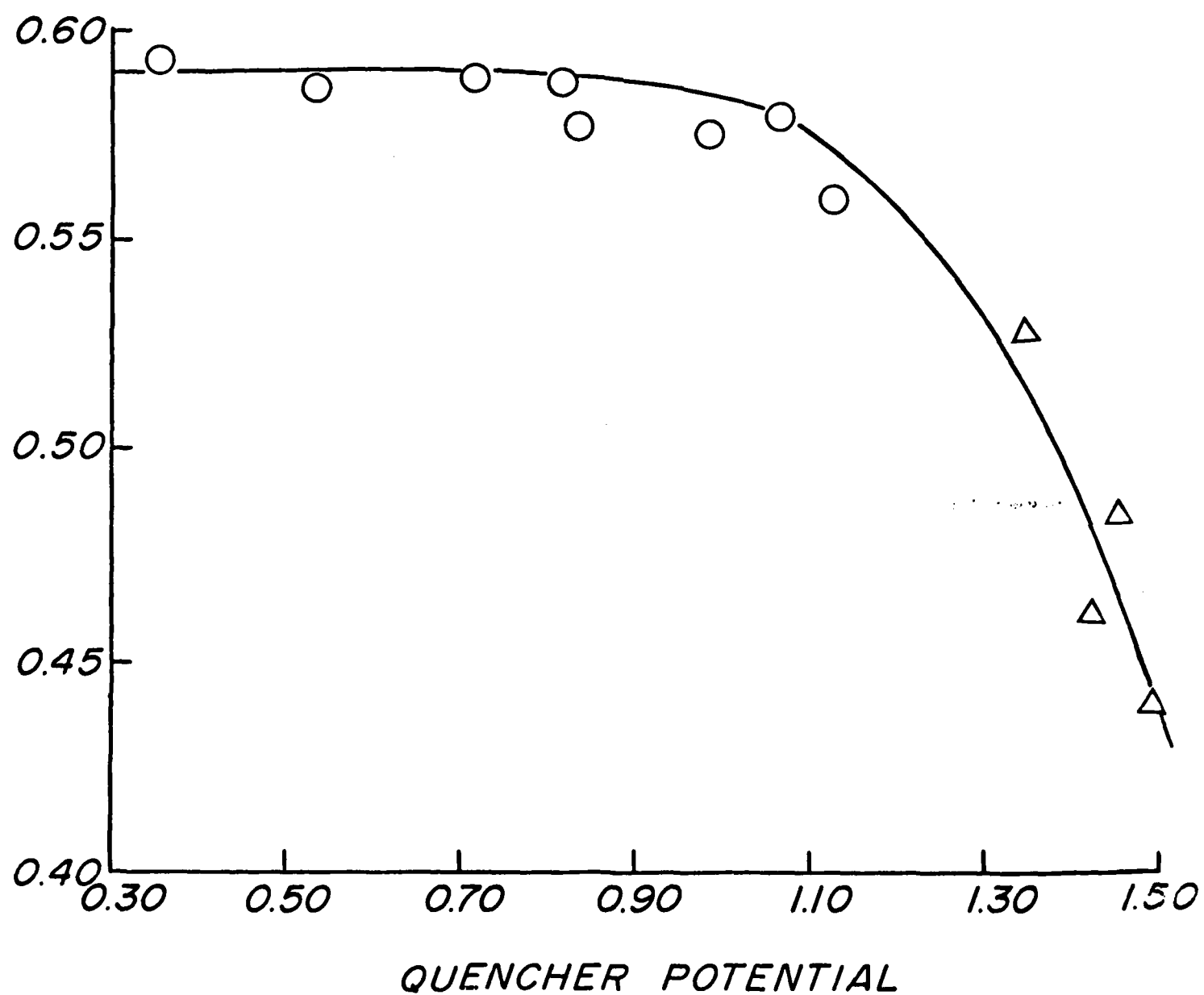
Table V Quenching Rate Constants for the $\text{Ru}(\text{bipy})_3^{2+}$ Ion^a

Quencher	Medium	$k_q \text{ M}^{-1}\text{s}^{-1}$	Ref.
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	0.5M H_2SO_4	2.7×10^9	24
	1.0M KCl	4.8×10^9	tw
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	1.0M KCl	3.3×10^6	tw
$\text{Cu}(\text{H}_2\text{O})_4^{2+}$	0.5M H_2SO_4	6.2×10^7	25
	1.0M KCl	8.3×10^8	tw
$\text{Co}(\text{NH}_3)_6^{3+}$	0.5M H_2SO_4	1×10^7	28
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	0.5M H_2SO_4	9.3×10^8	28
$\text{Fe}(\text{CN})_6^{4-}$	0.5M NaCl	49×10^8	27

a) Room temperature, uncorrected for diffusion. tw = this work

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Figure 1 A plot of $RT\ln k_q$ versus the quencher potential $E(Q^+/Q)$. The circles are experimental points, and the solid line is the theoretical line based upon eqn.(5), using the parameters presented in the text.



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